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Reflection properties of the 211 planes in calcite

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With 3 figures in the text

In connection with an investigation by Brogren and the author [1] of the reflection properties of the gratings commonly used in x-ray spectroscopy an investigation has been carried out for the 211 planes in calcite. A double crystal spectrometer has been used for the work. The investigation covered the wavelength range from 0558 x.u. to 5750 x.u., and measurements have been made of the per cent reflection, the double-crystal coefficient of reflection and the width of the rocking curve. The grating constant of the 211 planes is 3029 x.u. corresponding to a limiting wavelength of about 6000 x.u. in the first order of reflection, where all measurements have been made. Special attention has been paid to the wavelengths on each side of the *K* absorption edge of calcium.

The crystal specimens used in this investigation have also been used as monochromator crystals in an investigation by Brogren and the author [1] of the anomalous x-ray transmission in calcite in the wavelength range 1537–4420 x.u. with the interest focused especially on the conditions around the critical *K* absorption edge of calcium. In this connection it was of great importance to know if the monochromator used had the properties of a perfect crystal and particularly to know its properties for wavelengths around the absorption edge, where characteristic discontinuities could be expected in all three quantities, per cent reflection, double-crystal coefficient of reflection and width of the rocking curve. In earlier investigations of the reflection properties of calcite [2] (performed with an ionization chamber as a detector) an insufficient number of measuring points were taken in this region, which is the most interesting from the theoretical point of view.

In order to obtain a comparison with the prevailing theory a theoretical calculation has also been performed of the primary diffraction patterns and of the composed pattern in the (1, −1)-position for each of the wavelengths in question. From this were obtained the theoretical values of the three quantities under investigation. The tedious calculations have been performed with a BESK calculator by the Swedish Board for Computing Machinery.

Theory

The dynamic theory of x-ray diffraction in a perfect, absorbing crystal has been the basis of the theoretical calculations. Zachariasen's account of the dynamic theory [3] has been used and in most cases his notation has been adopted. A survey of the relevant parts of the theory has previously been given by Brogren and Adell [4].

Table 1. Parameters used in the calculation. For wavel

Wavelength λ x.u.	Bragg angle ϑ_B	Crystal structure factor F_{211}	$\varkappa$	Absorption coefficient μ_0 cm^{-1}	$\psi_0'' \times$
2558	25°00′	47.5 + i. 5.96	0.125	764	− 3.
2947	29°07′	43.1 + i. 7.46	0.173	1215	− 5.
3030	30°00′	39.9 + i. 7.80	0.196	1310	− 6.
3130	31°07′	40.8 + i. 0.336	0.00825	252	− 1.
3506	35°22′	44.6 + i. 0.420	0.00942	339	− 1.8
3864	39°38′	45.5 + i. 0.504	0.0111	449	− 2.
4420	46°53′	46.2 + i. 0.660	0.0143	640	− 4.
4700	50°53′	46.5 + i. 0.742	0.0160	780	− 5.8
5000	55°38′	46.7 + i. 0.836	0.0179	920	− 7.
5250	60°05′	46.8 + i. 0.918	0.0196	1040	− 8.
5550	66°22′	46.9 + i. 1.022	0.0218	1200	− 10.6
5750	71°40′	47.2 + i. 1.090	0.0231	1330	− 12.2

The primary diffraction pattern in the Bragg case is given by the expression

$$\frac{R_B(y)}{I} = L - \sqrt{L^2 - (1 + 4\varkappa^2)} \tag{1}$$

$$L = \sqrt{(-1 + y^2 - g^2)^2 + 4\,(g y - \varkappa)^2} + y^2 + g^2 \tag{2}$$

where $\varkappa$ is the ratio of the imaginary and the real parts of the crystal structure factor, g is a quantity proportional to the absorption coefficient, inversely proportional to the wavelength, the polarization factor and the real part of the structure factor. I is the intensity of the radiation incident on the crystal and y is an angular coordinate chosen so as to obtain about the same width of the diffraction pattern for every wavelength when expressed in terms of this angular coordinate.

Eq. (1) gives the intensity distribution of the parallelly or the perpendicularly polarized components of the reflected radiation for the two values of the polarization factor K. The incident radiation is assumed to be monochromatic and parallel. In a double crystal spectrometer the condition of monochromatism is realized for the radiation incident on the analyser crystal. The divergence of the beam is, however, determined by eq. (1). The radiation incident on the first crystal is completely unpolarized, hence the intensity distribution of the composed reflection pattern, the rocking curve, is given by the expression

$$R_{BB}(k) = \tfrac{1}{2} \int_{-\infty}^{+\infty} R_B^n(\vartheta)\, R_B^n(\vartheta - k)\, d\vartheta + \tfrac{1}{2} \int_{-\infty}^{+\infty} R_B^p(\vartheta)\, R_B^p(\vartheta - k)\, d\vartheta \tag{3}$$

where the angular coordinate k corresponds to the y-coordinate in eq. (1). Indices n and p indicate the perpendicularly and the parallelly polarized component, respectively. It appears that the rocking curve is obtained by folding the primary diffraction patterns of the crystal.

The per cent reflection P and the double-crystal coefficient of reflection R_D are given by n 0558 and 1932 x.u. the parameters are given in ref. [8].

$\times 10^6$	y_n		y_p		g_n	g_p
	rad. $\times 10^5$	sec.	rad. $\times 10^5$	sec.		
22.87	2.99	6.17	1.92	3.96	−0.136	−0.212
27.58	3.24	6.69	1.71	3.51	−0.207	−0.393
26.93	3.11	6.42	1.56	3.21	−0.235	−0.470
29.40	3.32	6.85	1.54	3.18	−0.0428	−0.0921
40.4	4.28	8.83	1.41	2.91	−0.0468	−0.142
50.0	5.09	10.50	0.952	1.96	−0.0552	−0.295
66.4	6.65	13.71	− 0.356	− 0.734	−0.0677	+1.266
75.5	7.72	15.9	− 1.57	− 3.24	−0.0773	+0.380
86.0	9.24	19.0	− 3.35	− 6.91	−0.0851	+0.235
95.0	11.00	22.7	− 5.53	−11.4	−0.0915	+0.182
106	14.42	29.8	− 9.80	−20.2	−0.1001	+0.148
115	19.25	39.7	−15.45	−31.9	−0.1060	+0.132

$$P = \frac{2\,R_{BB}(k)_{\max}}{\int_{-\infty}^{+\infty} R_B^n(y)\,dy + \int_{-\infty}^{+\infty} R_B^p(y)\,dy} \tag{4}$$

$$R_D = \frac{2\int_{-\infty}^{+\infty} R_{BB}(k)\,dk}{\int_{-\infty}^{+\infty} R_B^n(y)\,dy + \int_{-\infty}^{+\infty} R_B^p(y)\,dy}. \tag{5}$$

Calculations

The parameters used in the calculations are given in Table 1. The meanings of the symbols are given in Zachariasen's work [3]. The atomic structure factors are corrected for the anomalous scattering of the K electrons in accordance with the formulae given by Hönl [5, 6]. As the measurements have been performed in the first order of reflection exclusively the Debye-Waller factor has not been introduced, nor has any correction been applied for the scattering due to thermal vibrations.

Experimental part

The double crystal spectrometer used for the investigation was designed by Brogren, who will later publish a description of the apparatus as well as of the adjustment procedure. For most wavelengths the continuous x-radiation from tungsten was used. There was never any difficulty in obtaining sufficient intensity in spite of the fact that the high voltage was always kept below the threshold voltage of second order radiation. The use of a tungsten cathode prevented intensity variations due to the sputtering of the cathode material on the anticathode. For wavelengths where suitable x-ray lines were available, these were used for the adjustment. At the K absorp-

Table 2. Calculated and observed values of the half width of the rocking curve the per cent reflection and the double-crystal coefficient of reflection.

Wave-length. $\lambda_{\text{x.u.}}$	Width of rocking curve				Per cent refl.		Coeff. of refl.	
	Calc. $\omega_{\text{sec.}}$	Obs. $\omega_{\text{sec.}}$	Calc. $\omega_{\text{x.u.}}$	Obs. $\omega_{\text{x.u.}}$	Calc. P %	Obs. P %	Calc. $R \times 10^5$ rad.	Obs. $R \times 10^5$ rad.
0558	3.50		0.0514		80.0		1.60	
0708	4.45	5.2	0.0650	0.076	78.4	75	2.03	2.3
1081	6.90		0.100		74.0		2.91	
1274	8.17		0.118		72.3		3.37	
1537	9.60	10.8	0.136	0.153	69.8	68	3.88	4.2
1932	12.1	13.7	0.168	0.191	64.6	61	4.57	5.0
2558	16.1	17.3	0.215	0.230	57.1	54	5.45	5.6
2947	18.6	20.1	0.239	0.257	48.3	44	5.43	5.2
3030	18.4	18.8	0.233	0.239	45.8	43	5.17	4.6
3130	16.0	19.2	0.201	0.242	71.1	61	6.81	6.9
3506	21.3	25.6	0.262	0.305	70.2	60	9.02	8.8
3864	28.1	31.9	0.318	0.361	69.3	61	11.3	11.3
4420	39.4	42.7	0.396	0.430	64.0	57	14.6	13.5
4700	44.0	46.4	0.408	0.432	60.6	52	15.5	14.2
5000	48.5	53.9	0.402	0.447	58.4	49	16.9	15.0
5250	55.5	62.0	0.406	0.454	58.0	45	19.7	16.2
5550	75.6	82.5	0.444	0.484	57.9	45	26.3	21.1
5750	106	107	0.487	0.495	58.1	44	36.5	28.0

tion edge of calcium ($\lambda = 3064$ x.u.) special care was taken to obtain radiation of the right wavelength. Thus an adjustment was first made using the L_{α_1} radiation from tungsten in the second order, corresponding to a wavelength of 2947 x.u. in the first order of reflection. Then the high voltage of the x-ray tube was decreased and the measurements were performed with the continuous radiation. With this position of the crystals and the x-ray tube as a starting point the wavelength 3030 x.u. was obtained by an appropriate angular displacement of the x-ray tube, the crystals and the detector. A similar angular displacement gave the wavelength 3130 x. u. on the long wave side of the absorption edge.

The registration was made with a Geiger-Müller counter, filled with 100 mm of crypton and 10 mm of alcohol. With the aid of a revolving vacuum valve (of a new construction to be described by Brogren) in the lid of the spectrometer tank the Geiger tube could be adjusted to measure the radiation incident on the analyser crystal as well as the reflected radiation. The analyser crystal was turned until the face of the crystal plate was parallel to the beam leaving the monochromator. It was then brought out of the path of the beam with a revolving arm. Since the same counter was used for the registration of the direct intensity as well as of the reflected radiation, a comparison of the sensitivities of two different counters was avoided.

The Geiger counter window was a cellophane film, 20 μ thick and, for the softer radiation, a mylar film, 6 μ thick. The dead-time of the counter was determined and corrected for in the usual way. A number of controls were made during the investigation.

For the monochromator was used the same crystal as in the investigation of the anomalous x-ray transmission mentioned above. A similar crystal served as an analyser, both crystals being cut for Bragg reflection in the 211 planes. Before being

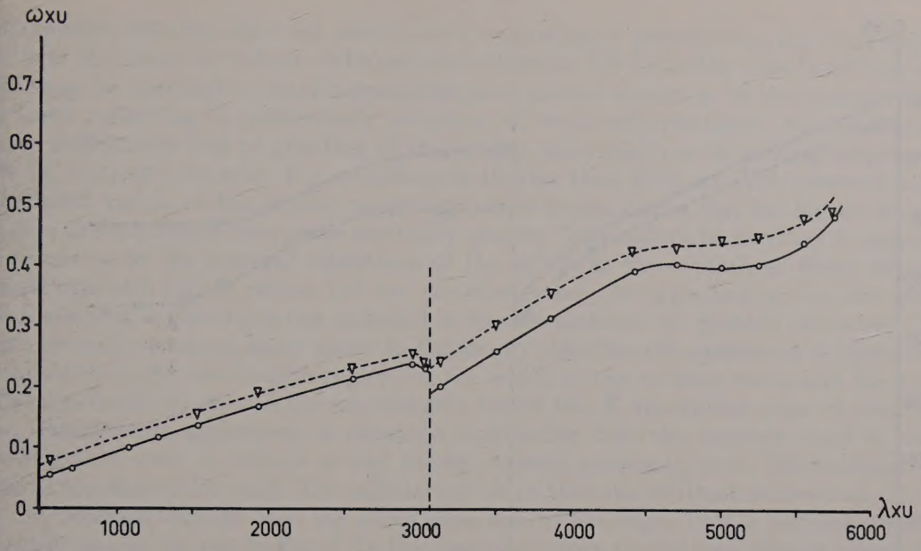

Fig. 1. Calculated (full line) and observed (dotted line) values of the width of the (1, –1) rocking curve.

used the crystal plates were etched in hydrochloric acid. The determination of the angle between the atomic planes and the crystal surface was performed in accordance with a method described by Brogren [7].

The crystals were adjusted for symmetric Bragg reflection in the (1, – 1)-position and the radiation reflected from the analyser crystal was measured in the region around the Bragg angle. Before and after the registration of each rocking curve the intensity of the radiation incident on the analyser was determined as described above. A 1 μ displacement of the precision screw that turned the analyser corresponded to a rotation of 0.9″ of this crystal. The half width was read off the rocking curve thus obtained. The value of the direct intensity, together with the peak height and the area of the rocking curve, which was evaluated by graphical integration, then gave the per cent reflection and the double-crystal coefficient of reflection. The background, the magnitude of which was about 70 counts per minute, was measured and subtracted from the counter readings. The lowest peak value obtained for the rocking curve was about 2000 counts per minute.

Recordings were made for wavelengths from the K_{α_1} line of Ag ($\lambda = 0558$ x.u.) and were extended to $\lambda = 5750$ x.u. At the K absorption edge of calcium measurements were made for $\lambda = 2947$, 3030 and 3130 x.u. as mentioned above. When all measurements were finished, a new registration was made with the copper line. No discrepancy with the first recording greater than the observational errors was obtained, indicating that the crystal properties had not changed during the investigation.

Results and discussion

In Table 2 and Figs. 1–3 are shown the results, both experimental and theoretical. The widths of the rocking curves are tabulated in x units as well as in seconds of arc in order to give a better conception of the resolving power of the crystal plane.

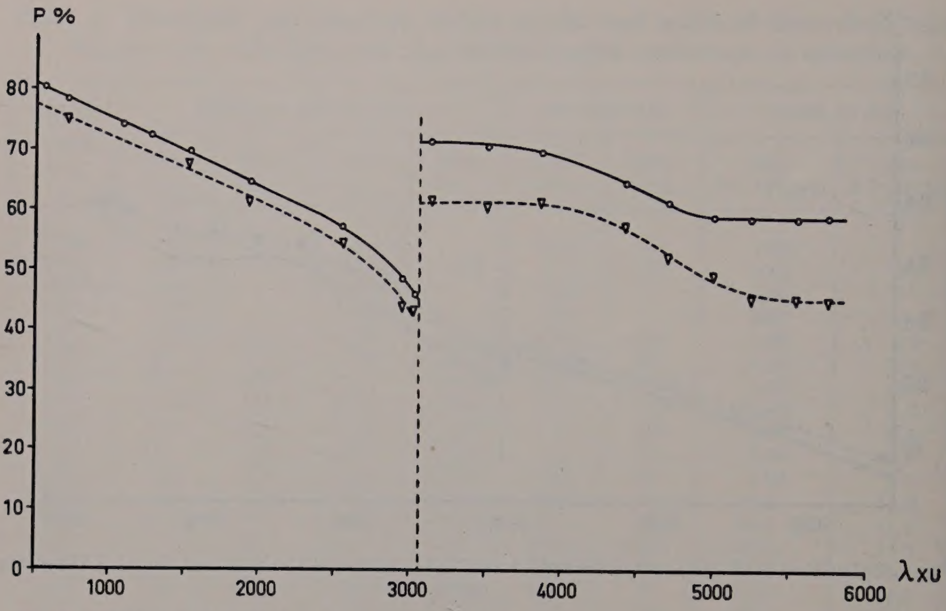

Fig. 2. Calculated (full line) and observed (dotted line) values of the per cent reflection.

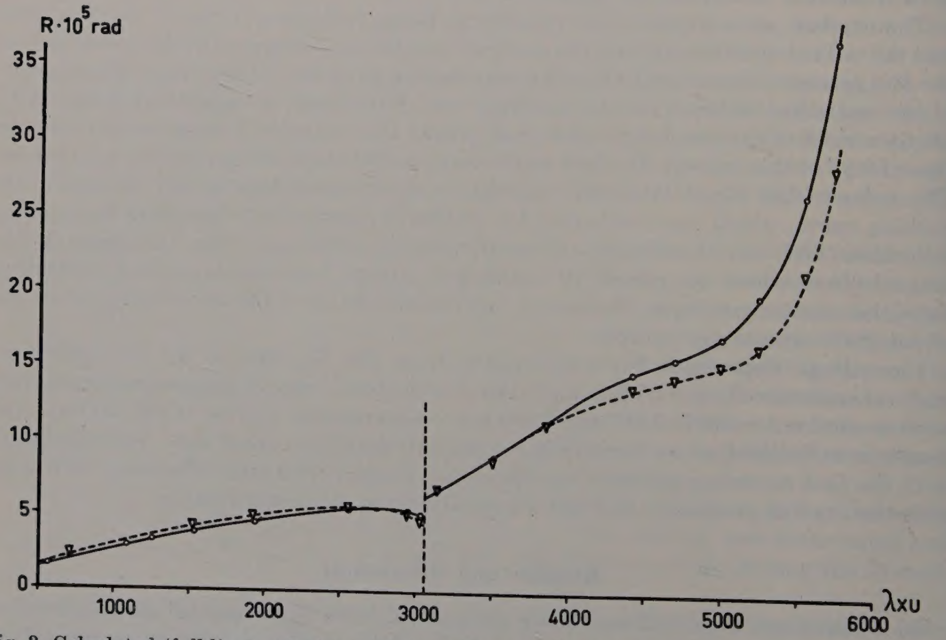

Fig. 3. Calculated (full line) and observed (dotted line) values of the double-crystal coefficient of reflection.

It appears that the observed widths are always slightly greater than the theoretical and that the observed values of the per cent reflection fall below the calculated values. This may be ascribed to small imperfections of mosaic structure in the crystal. The per cent reflection is particularly sensitive to such imperfections. As mentioned above deficiencies due to grinding of the surface were removed by etching both crystals in hydrochloric acid. For wavelengths shorter than 4000 x.u. the observed and calculated values of the crystal coefficient of reflection agree, but for longer wavelengths the calculated values are markedly greater. This cannot be ascribed to mosaic structure or to the thermal vibrations of the atoms in the crystal, as these effects should give still higher values, nor can the discrepancy be explained by the fact that the L electron scattering is not included in the calculations. As pointed out in ref. [2] there seems to be some inadequacy in the theory. Qualitative agreement is, however, obtained in every wavelength region for the width of the rocking curve and the two reflection coefficients, and for wavelengths below the K absorption edge of calcium also quantitative agreement is obtained, indicating that the crystals used in this investigation were as perfect as any calcite crystals previously used. Discontinuities arise at the absorption edge. The calculations show that the width of the rocking curve should decrease slightly near the short wave side of the edge. This is verified experimentally as can be seen in Fig. 1. In this case the theory thus gives a detailed description of the diffraction process in the crystal. The observation that the width of the $(1, -1)$ rocking curve decreases near the absorption edge of one of the elements in the crystal has also been made for the quartz plane $10\bar{1}0$ [1].

Also, for the reflection coefficients, P and R_D, calculations and observations agree in the region around the K absorption edge. Thus the crystals were well suited to be used as monochromators in the investigation of the anomalous x-ray transmission in this region.

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